New Electrochemical Preparation of Reactive Zinc with a Large Surface Area

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Reactive zinc was readily prepared by electrolysis of a DMF solution containing 0.1M Et_4NClO_4 using a platinum cathode and a zinc anode. Characterization of the zinc metal showed that it was an aggregation of very fine, crystalline zinc particles with a specific surface area of 24 m^2/g, which is 100 times larger than that of commercial zinc metals. Preparation of zinc with a much larger surface area of 56 m^2/g could be achieved by electrolysis of the solution at a lower current density.

Various methods of zinc activation, such as the reduction of zinc halide with alkaline metal or alkali metal naphthalenide, have been reported.[1] These methods, however, require high temperatures and long reaction times, or vigorous stirring during the reaction. Perichon and colleagues recently reported the preparation of a small amount of reactive zinc by a cathodic reduction of zinc bromide in acetonitrile, and carried out the Blaise reaction in the presence of a catalytic amount of the reactive zinc under electrolytic or nonelectrolytic conditions.[2] We have also reported a new method for preparation of reactive zinc by electrolysis and its use in facile isoprenylation of aldehydes and ketones.[3] The zinc thus prepared was shown to have a much higher reactivity in the isoprenylation than that of commercial zinc metals. Therefore, we carried out a study to characterize electrochemically generated reactive zinc by the use of various analytical methods. In this paper, we report the preparation of a very pure and reactive zinc metal with a large surface area.

Reactive zinc metal was readily prepared by electrolysis of a DMF solution containing 0.1M Et_4NClO_4 in a one-compartment cell fitted with a platinum plate cathode (2x2 cm^2) and a zinc plate (2x2 cm^2). Electrolysis was carried out at a constant current of 30 mA/cm^2 at room temperature in a nitrogen atmosphere. The electrolysis resulted in an anodic dissolution of the zinc anode to give zinc ions, which were reduced at the platinum cathode to give a zero valent reactive zinc. Electrogenerated reactive zinc (EGZn) was initially deposited on the platinum cathode and dispersed in a DMF solution at the end of the electrolysis. A solution containing EGZn could be used directly in various organic reactions after the zinc anode was removed from the electrochemical cell. Alternatively, the isolated EGZn could be used in the reaction after it was isolated. Isolation was carried out by filtration of the electrolyzed solution followed by washing with water, methanol and diethyl ether, and then drying. The isolated reactive zinc metal was then subjected to characterization.

$$\textbf{Pt cathode - Zn anode} \xrightarrow[\textbf{DMF}]{\textbf{\textit{electrolysis}}} \textbf{"Zn" (EGZn)}$$

Characterization of the electrogenerated reactive zinc (EGZn) and commercially available zinc metals was carried out by scanning electron microscopic analysis (FE-SEM), X-ray diffraction, B.E.T. surface area analysis, X-ray photoelectron spectroscopy (XPS), and fluorescent X-ray spectroscopy. The representative results are summarized in Table 1. FE-SEM photographs of EGZn and one of the commercially available zinc powders (E. Merck) are shown in Figures 1(a) and 1(b). These analyses show that the EGZn is an aggregation of very fine particles (less than 0.1 μm in diameter), whereas the particle size of six kinds of commercially available zinc metals is 2-400 μm in diameter. The specific surface area of the EGZn was found to be 24 m^2/g, which is hundred times larger than that of commercial zinc metals. X-Ray diffraction of EGZn showed a hexagonal crystal structure, which is a typical crystal form of the zinc metal. X-Ray diffraction also showed that the crystal size of the EGZn is smaller than that of commercial zinc metals since the width of half height of the diffraction peaks in the EGZn was broader than those of commercial zinc metals.

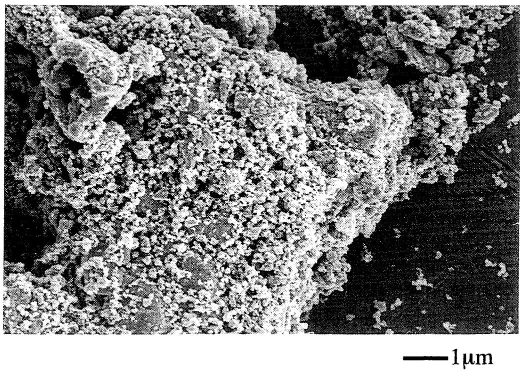
Recently, it was reported by Takai, Utimoto, and colleagues that a trace amount of lead in zinc metal retards the Simmons-Smith reaction using diiodomethane[4a] or, in some cases, promotes Wittig-type olefination.[4b] We also examined the contents of impurities in EGZn and commercial zinc metals. Fluorescent X-ray spectroscopy and XPS showed that the EGZn was a very pure zinc metal, containing no impurities such as lead, chloride ions or nitrogen compounds in contrast to commercial zinc metals which contain 0.01-0.03 mol% of lead (Table 1).

A much higher reactivity of EGZn than that of commercial zinc metals was shown by isoprenylation[3] and allylation[5] of ketones and aldehydes. It is very likely that this high reactivity of EGZn is attributable to the large surface area of the metal. There-

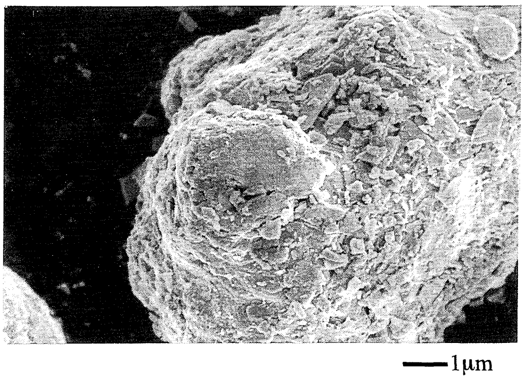
Table 1. Characterization of various zinc metals

Run	Zinc metal	Particle size[a] (μm)	Specific suface area[b] (m^2/g)	Content of lead[c] (mol% of zinc)
1.	EGZn	<0.1	23.8	0
2.	E. Merck	5-15	1.9	0.01
3.	Aldrich Chemical	50-150	0.4	—[d]
4.	Rare Metallic	100-400	0.5	0.01
5.	Wako Pure Chemical	2-8	2.5	0.03
6.	Nacalai Tesque	3-9	1.3	—[d]
7.	Kanto Chemical	3-10	0.8	—[d]

[a]Estimated by FE-SEM photographs. [b]Measured by B.E.T. surface area analysis. [c]Measured by fluorescent X-ray analysis. [d]Not determined.



(a) EGZn



(b) E. Merck

Figure 1. FE-SEM photographs of the electrogenerated reactive zinc (EGZn) (a) and E. Merck zinc powder (b).

fore, we attempted to prepare EGZn with a much larger surface area, and were able to accomplish this by electrolysis at a lower current density. Electrolysis of a DMF solution at a lower current density produced a reactive zinc metal with a larger surface area. The results are shown in Figure 2. EGZn with a specific surface area of 56 m^2/g could be prepared by electrolysis at a constant current of 2.5 mA/cm^2.

The EGZn with a larger surface area exhibitted a higher reactivity in the prenylation of benzoic anhydride (Scheme 1). Prenylation of benzoic anhydride with 1-chloro-3-methyl-2-butene (**1**) was carried out in a DMF solution by using two kinds of EGZn with specific surface areas of 6 (EGZn-A) and 20 m^2/g (EGZn-B). The reaction of **1** with benzoic anhydride in the presence of EGZn-A and EGZn-B at room temperature for 5 min gave 2,2-dimethyl-1-phenyl-3-buten-1-one (**2**) in yields of 18 and 48%, respectively, and the reaction for 60 min gave **2** in yields of 72 and 95%, respectively.

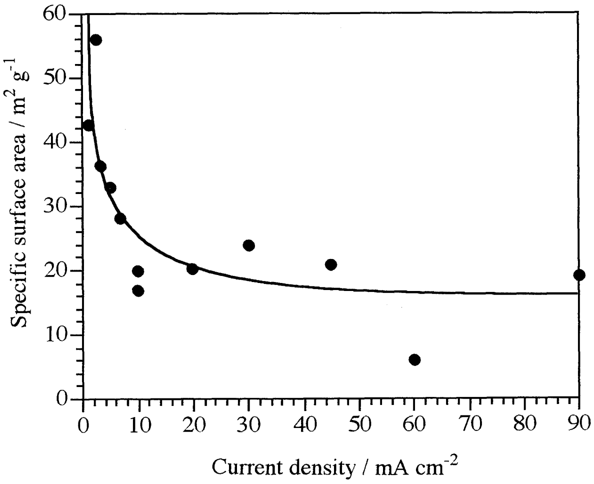
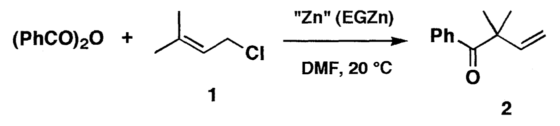


Figure 2. Effect of current density on specific surface area of the electrogenerated reactive zinc (EGZn).



Scheme 1.

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References and Notes

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